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ABSTRACT

A highly selective, controlled-potential coulometric method has been developed for the determination of plutonium. An automated instrument, consisting of commercial electronic components under control of a programmable calculator, is being constructed.

INTRODUCTION

A series of automated instruments is being developed for the determination of uranium and plutonium. The first instrument in this series, an automated spectrophotometer for the determination of both uranium and plutonium, has been described in another paper¹ presented in this conference. A second automated instrument, for the controlled potential coulometric determination of plutonium, is under construction. Like the automated spectrophotometer, it will feature high tolerance to impurity elements present in nuclear fuel cycle materials and measurement of low-milligram levels of plutonium. The expected measurement precision is 0.1-0.2% relative standard deviation, about five times better than is obtained with the automated spectrophotometer. Analysis time per sample will range from about 15 to 30 minutes contrasted to five minutes for the automated spectrophotometer.

This paper describes a versatile apparatus using commercial components that has been assembled for the investigation of electrometric titration systems, the development of a highly specific, controlled-potential coulometric method for plutonium, and the construction status of the automated instrument that will incorporate many of the components of the versatile apparatus.

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VERSATILE APPARATUS FOR INVESTIGATING ELECTROMETRIC TITRATION SYSTEMS

This apparatus, consisting of commercial components, is centered around a Princeton Applied Research Corporation 173D Potentiostat-Galvanostat (having a compliance voltage of ± 100 at currents up to 1 A) and 179D Digital Coulometer (having an integration reproducibility of 0.02% full scale) that are interfaced to a Hewlett-Packard 9825A Programmable Calculator. Interfaced and under control of the calculator are a scanner, digital multimeter, a digital-to-analog converter, a clock, and a digital plotter, as shown in Fig. 1. The calculator controls most functions of the potentiostat and the coulometer, and receives and processes data from them.

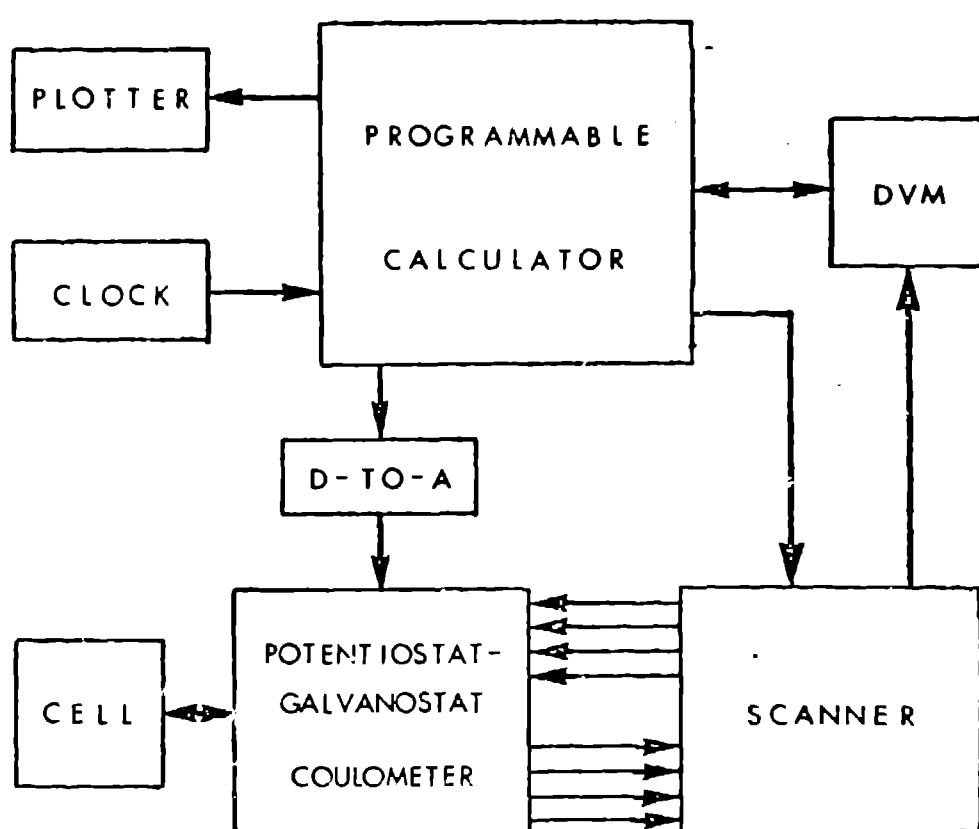


Fig. 1. Versatile electroanalytical apparatus.

Controlled potential or controlled current titrations are done with the calculator establishing and controlling electrolysis conditions and monitoring the variables of interest such as current, voltage, coulombs, and time. The output data can be processed on-line, decisions made, and conditions adjusted, or the data can be stored on a magnetic tape cassette for later analysis. The digital multimeter measures the desired variable as selected by the scanner. The digital-to-analog converter provides capability (to the calculator) to select a desired electrode potential when operating in the controlled-potential mode or the current when operating in the controlled-current mode. During all phases of an electrolysis, the on-line digital plotter records the variables of interest, usually a plot of \log_{10} current vs time or electrode potential vs time.

The calculator uses a simple, high-level language and programs are easily changed. This flexibility provides capability to thoroughly evaluate the many factors that influence an electrotitration. For example, one program carries out a controlled potential coulometric titration involving reduction at a set potential and sequential oxidation at two different potentials. The controlled operational sequence includes (1) clearing the coulometer, (2) setting the reduction electrode potential, (3) electrolysis to a selected background current level, (4) outputting coulombs, (5) resetting the coulometer, (6) setting the first oxidation potential, (7) electrolyzing to a selected background-current-level endpoint, (8) outputting coulombs, (9, 10, 11, 12) repeating (5, 6, 7, and 8) for the second oxidation, and (13) stopping the electrolysis. The electrolysis can be interrupted at any time for manual operation and can be returned to any point in the calculator-controlled mode.

CONTROLLED-POTENTIAL COULOMETRIC METHOD FOR PLUTONIUM DETERMINATION

A method has been developed that features high specificity, a precision of 0.1 to 0.2% relative standard deviation at the 5-mg plutonium level, and operational simplicity for adaptation to an automated instrument. Plutonium is reduced to Pu(III) in HCl-sulfamic acid electrolyte, diverse ions are oxidized at a potential below where Pu(III) is significantly oxidized, phosphate is added to lower the Pu(III)-Pu(IV) potential, and Pu(III) is titri-

metrically oxidized to Pu(IV). The scheme was suggested by a recent paper² which described a potentiometric titration in which the reduction and oxidations were done chemically.

Table 1 summarizes the half-cell potentials of Pu(III)-Pu(IV) and Fe(II)-Fe(III) as a function of HCl molarity, measured using the apparatus described previously. The maximum difference of about 0.32 V in these half-cell potentials is essentially constant over the HCl molarity range of about 5 to 7.4. This difference is ample so that iron, a troublesome interference in most plutonium electro-metric methods, can be oxidized with little oxidation of plutonium. The 5.5 M HCl level was selected for the electrolyte. The apparent advantage of lower values for both half-cell potentials at higher HCl concentrations is more than offset by increased background currents from electrolysis of HCl. A potential of 0.57 V (all electrode potentials are vs SCE) was selected for the initial oxidation at which > 99.99% of the iron and 0.25% of the plutonium is oxidized.

For oxidation of Pu(III) to Pu(IV), a complexant must be added to reduce the half-cell potential to below the

Table 1. HALF-CELL POTENTIALS OF Pu(III)-Pu(IV) AND Fe(II)-Fe(III) IN HCl

HCl Molarity	Half-Cell Potentials (vs SCE)		
	<u>Pu(III)-Pu(IV)</u>	<u>Fe(II)-Fe(III)</u>	<u>Difference</u>
2.5	0.705	0.446	0.259
4.7	0.701	0.397	0.304
5.5	0.686	0.372	0.314
5.8	0.686	0.371	0.315
6.6	0.662	0.343	0.319
7.0	0.649	0.332	0.317
7.4	0.640	0.323	0.317

level where HCl oxidizes. Of various reagents evaluated, phosphate, added as NaH_2PO_4 , was most effective. In 5.5M HCl containing 1M NaH_2PO_4 , the Pu(III)-Pu(IV) half-cell potential is lowered to 0.50 V and > 99.9% oxidation is attained at 0.68 V with insignificant oxidation of HCl.

Selected operating conditions for the method are 10 ml of 5.5M HCl-0.015M sulfamic acid (added to increase tolerance to HNO_3) electrolyte, an initial reduction at 0.25 V, an oxidation of diverse ions at 0.57 V, addition of 2.5 ml of 5M NaH_2PO_4 , and oxidation of Pu(III) to Pu(IV) at 0.68 V. A current endpoint of 50 μA is used for all three electrolyses. To attain highest reliability, background corrections are established by blank electrolyses using the same time durations as for samples.

Detailed investigations of diverse ion effects are summarized in Fig. 2 for 50 metal cations and in Table 2 for 24 nonmetal and three metal anions.

H	★ NO INTERFERENCE AT 1:1 MOLE RATIO																				
Li	Bo	•• NO INTERFERENCE AT 1:10 MOLE RATIO															B	C	N	O	F
Na	Mg	≡ INTERFERED AT 1:10 MOLE RATIO															Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I					
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At					
Fr	Ra	Ac																			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					

Fig. 2. Metal cations interference effects.

TABLE 2
ANION INTERFERENCE EFFECTS

<u>Nonmetal Anion</u>	<u>Highest Mole Ratio^a Tested with No In- terference</u>	<u>Nonmetal Anion</u>	<u>Highest Mole Ratio,^a Tested with No In- terference</u>
Acetate	500	I ⁻	50
Borate	500	IO ₃ ⁻	< 5
Br ⁻	5	NO ₃ ⁻	50 ^b
BrO ₃ ⁻	< 5	Oxalate	< 5
Citrate	500	PO ₄ ³⁻	< 25
Cl ⁻	500	S ²⁻	< 5
ClO ₃ ⁻	< 5	SO ₃ ²⁻	< 5
ClO ₄ ⁻	500	SO ₄ ²⁻	50
EDTA	500	S ₂ O ₃ ²⁻	< 5
F ⁻	< 5	S ₂ O ₈ ²⁻	5
Formate	500	SCN ⁻	< 5
H ₂ O ₂	50	Tartrate	50

<u>Metal ion</u>	<u>Highest Mole Ratio^a Tested with No In- terference</u>
MnO ₄ ⁻	1
MoO ₄ ⁻²	1
VO ₃ ⁻	1

^a Mole ratio relative to plutonium, plutonium level = 0.02 millimole (5 mg). A < 5 value means interference at this level.

^b Not tested at 500 mole ratio because of possible degradation of platinum gauze working electrode by HCl-HNO₃ mixture.

No metal cation normally present in nuclear fuel cycle material interferes (defined as a change significant at the 95% significance level relative to plutonium alone) at an equal mole ratio relative to 0.02 millimole (5 mg) of plutonium. Only four metals, antimony, gold, iridium, and selenium, interfere at a 0.1-mole ratio. These oxidize at the 0.68-V measurement potential to cause positive bias. Tungsten and thallium partially oxidize at 0.68 V, producing positive bias at an equal mole ratio, but no effect at a 0.1-mole ratio. Platinum, the working electrode material, unexpectedly interferes giving a positive bias. Zirconium and hafnium precipitate as phosphates that partially occlude plutonium to cause negative bias at an equal mole ratio. At a 0.1-mole ratio, the effect is not significant. All members of the alkali, alkaline earth, and lanthanide groups were not tested. Results for representative members are considered to apply to all members. Cerium and europium were tested because they have oxidation states, Ce(IV) and Eu(II), other than (III).

Nonmetal anions were tested first at a 500 mole ratio relative to plutonium, at a plutonium level of 0.02 millimole (5 mg). If there was a significant effect, lower mole ratios of 50 and then 5 were tested. The three metal anions were tested at an equal mole ratio. Most interfering nonmetal ions are effectively removed by perchloric acid fuming, successfully shown for Br^- , BrO_3^- , ClO_3^- , F^- , H_2O_2 , I^- , IO_3^- , NO_3^- , S^{2-} , SO_3^{2-} , and SCN^- .

Contrary to what generally is believed, the reduction of Pu(VI) to Pu(III) is rapid (at 0.25 V) in the HCl-sulfamic acid electrolyte. The method therefore applies to the determination of total plutonium present in all its oxidation states.

The diverse ion interference study subjected the platinum gauze working electrode to rough treatments without serious effect. The background currents for reduction and both oxidations remained satisfactorily low. The only adverse effect was an increase in electrolysis time, especially for the 0.68-V plutonium oxidation, which increased about twofold. Normal performance is restored by a simple treatment of sequential immersions in hot 16M HNO_3 , water, and 12M HCl .

STATUS OF AUTOMATED INSTRUMENT

Construction of an automated instrument is underway. The electronic components are essentially the same as described previously for the versatile apparatus. The potentiostat is modified for external control of the selector switch by the programmable calculator.

A 49-cm-diam turntable, holding up to 24 electrolysis cells, rotates the cells into position under a fixed Teflon support. This support holds the electrodes, stirrer, and tubes that deliver reagents, rinsing solution, and nitrogen gas. A pneumatically driven cylinder will raise a simple cylindrical cell into position against the Teflon support, forming an air-tight seal. The lifting mechanism has been satisfactorily tested.

Vigorous, yet reproducible stirring is necessary to attain fast and precise electrolyses. This is provided by a glass paddle that is rotated at 1800 rpm through a close-fitting hole in the Teflon support.

The reagent dispensers, syringes driven by a combined hydraulic-pneumatic system, are patterned after those used with the automated spectrophotometer.³ Only glass, Teflon, and Kel-F contact the corrosive reagents. Their construction and testing is complete.

REFERENCES

1. D. D. Jackson, R. M. Hollen, S. F. Marsh, M. R. Ortiz, and J. E. Rein, "Determination of Submilligram Amounts of Uranium with the LASL Automated Spectrophotometer," Twenty-First Conference on Analytical Chemistry in Energy Technology Proceedings, ORNL, October 4 - 6, 1977, Gatlinburg, TN.
2. W. Davies and M. Townsend, United Kingdom Atomic Energy Authority report TRG-2463 (1974).
3. D. D. Jackson, D. J. Hodgkins, R. M. Hollen, and J. E. Rein, Los Alamos Scientific Laboratory report LA-6091 (February 1976).